Spectroscopic and cyclic voltammetric studies of poly(*p*-phenylene vinylene) prepared from two different sulphonium salt precursor polymers

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Films of poly(*p*-phenylene vinylene) (PPV) were prepared by thermal elimination reactions of two different sulphonium salt precursor polymers. The ultra-violet/visible (u.v./vis.), fluorescence and Raman spectra and small-angle X-ray scattering diagrams of each PPV sample were compared, and the oxidation and reduction potentials of each PPV were determined by cyclic voltammetry. The u.v./vis. spectra of PPV films made from a sulphonium salt polymer based on a cyclic sulphide, which was converted to PPV at a temperature about 100°C lower than that required to obtain PPV from an acyclic sulphide sulphonium salt polymer, showed phonon sidebands at room temperature as well as at −200°C. The phonon sidebands were apparently associated with a narrower distribution of crystallite sizes (with an average long period spacing of 300 Å), which was obtained when PPV was made from the cyclic sulphonium chloride precursor polymer. The experimental values for the oxidation and reduction potentials and for the band gap were found to be in good agreement with the values predicted by *ab initio* calculations and from previous literature reports. The oxidation potential was found to be 0.80 V vs. SCE (saturated calomel electrode), the reduction potential was found to be −1.8 V vs. SCE, and the band-gap energy was found to be around 2.4 eV. The high value for the oxidation potential for PPV, in comparison to the oxidation potential of triiodide (0.52 V vs. SCE), from which an approximate value of 2×10^{-10} for the oxidation constant was obtained, explains why only very low conductivities were obtained when PPV was 'doped' with iodine.

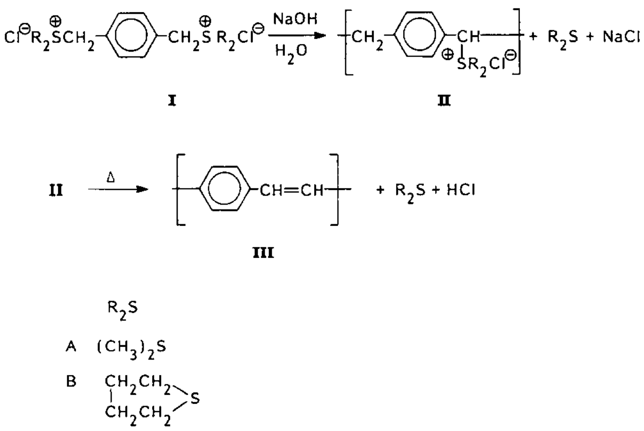
(Keywords: spectroscopy; poly(*p*-phenylene vinylene); cyclic voltammetry)

INTRODUCTION

Poly(*p*-phenylene vinylene) (PPV), **III**, can be prepared from a high-molecular-weight water-soluble precursor polymer, **II**, by a synthetic route first described by Wessling and Zimmerman[1]. The solubility and high molecular weight of the precursor polymer allow PPV to be obtained as a high-molecular-weight polymer in film form. The precursor is readily prepared in aqueous solution at low temperature through the polymerization of a bis-sulphonium salt of *p*-xylene, **I**, by reaction with sodium hydroxide. The mehanism of the polymerization reaction is not understood and is under investigation in our laboratory. The two reactions involved in the synthesis of **III** are shown in **Scheme 1**.

Lenz and coworkers[2] have shown that the use of cyclic sulphides, such as **IB**, in the reaction sequence leads to higher yields and higher molecular weights for the preparation of **II** and to more efficient elimination reactions in the conversion of **II** to **III**. Indeed, there are some discrepancies between the expected and experimental u.v./vis. spectra for **III** prepared from the precursor based on the acyclic sulphide, **IA**. Most likely, side-reactions and/or residual impurities are responsible for these differences. In the present study, ultra-violet/visible, Raman and fluorescence spectra and small-angle X-ray scattering patterns were compared for **III** prepared from acyclic, **IA** and **IIA**, and cyclic, **IB** and **IIB**, sulphonium salt monomers and precursor polymers.

A second objective of the present study was to examine the cause of the low conductivities obtained when **III** is doped with iodine[3–6]. It has been suggested that the poor conductivity is caused by either the high ionization potential (oxidation potential) of **III** or the inability of iodine to diffuse into the polymer film.



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The theoretical values for the oxidation and reduction potentials of **III** are +0.70 and −1.80 V compared to the saturated calomel electrode (SCE), according to the values for the ionization potential and electron affinity calculated by Bredas and coworkers[4]. The oxidation potential, E_{ox}, and the reduction potential, E_{red}, can be calculated from the ionization potential, E_I, and electron affinity, E_A, by the following equations:

$$E_{ox} = (E_I + 1.9 - 6.3)\ \mathrm{V}$$

$$E_{red} = (E_I - E_A + 1.9 + 6.3)\ \mathrm{V}$$

Obzrut and Karasz[7] have recently reported an oxidation potential of 3.85 V vs. a lithium electrode for **III** made from the **IIA** precursor polymer, and Hörhold and coworkers[8] have reported values of 0.76 and −1.74 V vs. Ag/AgCl for the oxidation and reduction potentials of **III** made from the **IIA** precursor.

A comparison of the oxidation potentials for **III** prepared from each type of precursor to the oxidation potential of iodide and triiodide could provide an insight into the cause of the very low conductivities that are obtained when **III** is 'doped' with iodine. It would also be of interest, of course, to compare the experimental values of the oxidation potentials with the theoretical values[4].

In this report, the u.v./vis., fluorescence and Raman spectra and the small-sngle X-ray scattering patterns of **III**, which was prepared from the dimethylsulphonium chloride precursor polymer, **IIA**, and from the tetramethylenesulphonium chloride precursor polymer, **IIB**, were compared. The spectra were also compared with spectra of well defined oligomers of **III** reported by Drefahl and coworkers[9] and with the spectra reported by Obzrut and Karasz[10]. Cyclic voltammetry was used to determine the oxidation and reduction potentials of **III** obtained from each precursor, and an explanation for the low conductivities of iodine-treated PPV is presented.

EXPERIMENTAL

Polymer synthesis

Aqueous solutions of the precursor polymers **IIA** and **IIB** were obtained from monomers **IA** and **IB** according to methods described by Lenz and coworkers[2,3]. For the cast films of the **IIA** precursor polymer, a total conversion to **III** required a thermal treatment at 330°C for 24 h *in vacuo*[3,11], while for the **IIB** precursor polymer, the total conversion to **III** could be achieved at only 240°C for 24 h *in vacuo*[2]. Total conversion in this report is defined as the thermal treatment temperature after which the elements sulphur and chlorine are undetectable (less than 0.1%).

Polymer characterization

Intrinsic viscosities were measured at 20°C using a Schott Ubbelohde Type I Viscometer with two optical beams used to measure the flow times of the solutions and with a 0.05 M sodium sulphate solution as the solvent. I.r. and fluorescence spectra were taken on fully converted cast films. Samples for u.v./vis. and Raman spectroscopy were made by casting thin films onto quartz substrates and converting the sample to poly(phenylene vinylene), **III**, by the appropriate conditions described in the previous section. I.r. spectra were obtained on a Nicolet 60SX Spectrophotometer. U.v./vis. spectra were obtained on a Perkin–Elmer Lambda 9 UV/VIS/NIR spectrophotometer. Fluorescence spectra were obtained on a Spex Fluorolog with a 450 W xenon lamp using wavelengths of 420, 400, 370 and 313 nm. Raman spectroscopy was performed on a Spex spectrometer using an excitation wavelength of 647 nm.

Cyclic voltammetry

Cyclic voltammetry was performed under highly pure conditions using the equipment described by Heinze[12]. Films were cast upon the positive (working) electrode by adding about 0.01 ml of prepolymer solution (dilute solution in the case of thinner films) and heating under vacuum at the appropriate temperature.

The cyclic voltammograms were performed against a Ag/AgCl reference electrode under inert conditions using dried dichloromethane or acetonitrile (dichloromethane could not be used for reductions) as the solvent with t-butylammonium perchlorate as the supporting electrolyte. The scan speed was varied between 1 and 100 mV s^{-1}. The electrochemical cells were calibrated by using a ferrocene standard[13].

RESULTS AND DISCUSSION

The polymer yields, intrinsic viscosities of the precursor polymers **IIA** and **IIB**, as shown in *Table 1*, and the i.r. spectra of the fully converted phenylene vinylene polymers from both precursors are consistent with previous reports[2,3]. The u.v./vis. spectra of **III** made from the two precursor polymers **IIA** and **IIB** are given in *Figure 1*. The u.v./vis. spectrum of **III** made by the precursor polymer **IIA** is in good agreement with previous reports, and the absorption edge of the spectrum for **III** made from both precursor polymers is in good agreement with the absorption edge calculated by Drefahl and coworkers[9]. However, the u.v./vis. spectrum of **III** made from the precursor polymer **IIB** is markedly different from all of the previously reported u.v./vis. spectra for PPV. In particular, the spectrum shows phonon sidebands even at room temperature with discernible maxima at 20220, 21740 and 23000 ± 100 cm^{-1}, and the experimental band gap of 2.4 eV (19700 cm^{-1}) is in excellent agreement with the band gap of 2.5 eV (20180 cm^{-1}) predicted by Bredas and coworkers[4].

Table 1 Yields and viscosities for the polymerization reactions of the bis-sulphonium salt monomers[a]

Monomer	Concentration (M)	Polymer yield (%)[b]	$[\eta]$ (dl g^{-1})
IA	0.2	16	2.34[c]
	0.2	15	3.0[d]
IB	0.2	38	5.2[c]
	0.2	36	6.0[d]

[a] All reactions were run in aqueous solution under an inert atmosphere at 0°C for 30 min

[b] Determined gravimetrically from the concentration of polymer in the dialysed solution after evaporation and conversion to polymer **III**

[c] Intrinsic viscosities reported in ref. 2 for water/methanol (4/1 by volume) solutions of polymers **IIA** and **IIB** containing 0.05 M Na_2SO_4 at 25°C

[d] Intrinsic viscosities determined in this study for water solutions of polymers **IIA** and **IIB** containing 0.05 M Na_2SO_4 at 20°C

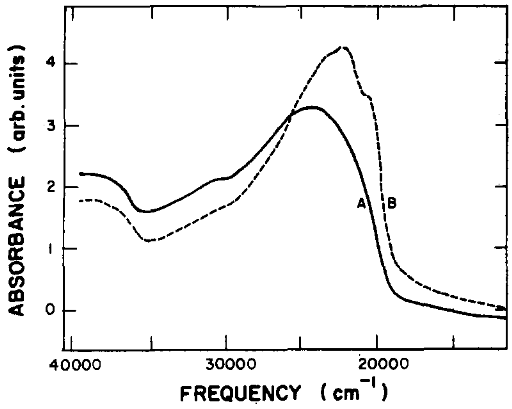

Figure 1 U.v./vis. spectrum of PPV, **III**, made from (A) the acyclic sulphonium salt precursor polymer **IIA** and (B) the cyclic sulphonium salt precursor polymer **IIB**

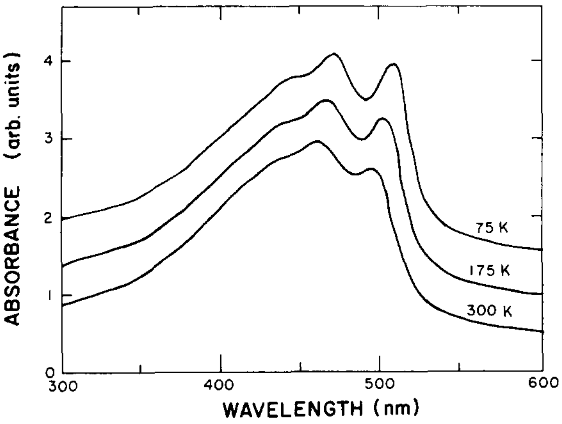

Figure 2 U.v./vis. spectrum of PPV, **III**, made from the cyclic sulphonium salt precursor polymer **IIB** at 300, 175 and 75 K. (Note that the spectra are shifted vertically for clarity)

As shown in *Figure 2*, the phonon sidebands are even more sharply defined at 75 K with peaks at 19 770, 21 310 and 22 550 ± 100 cm^{-1}. This result suggests that there are little or no side-reactions which would disrupt the polymer structure involved in the conversion of the precursor polymer, **IIB**, to PPV. Each number of uninterrupted arylene vinylene repeat units (conjugation length) has a characteristic electronic π–π^* transition. The greater the number of uninterrupted arylene vinylene repeat units (longer conjugation length), the lower the energy of this transition. If a polymer had a broad distribution of uninterrupted repeat units (conjugation lengths), such as that prepared from precursor **IIA**, the overlapping of the absorption spectrum from each of the different uninterrupted repeat units would wash out the phonon structure. The phonon sidebands were found only in stretched films of the PPV obtained from the precursor polymer **IIB**.

Further supporting evidence for the assignment of the peaks to phonon sidebands is shown in the fluorescence spectra of PPV shown in *Figure 3*. The fluorescence spectra for PPV made from both precursors were found to be identical, along with all other spectra taken at different excitation wavelengths. By the use of peak-resolving methods, the fluorescence spectrum for PPV made from both precursors was found to have peaks at 19 420, 17 920 and 16 690 ± 100 cm^{-1}. The differences in energy between neighbouring peaks in the fluorescence spectrum are similar to the differences in energy between neighbouring peaks in the u.v./vis. spectrum for PPV made from the precursor polymer **IIB** (1530 and 1250 ± 100 cm^{-1} for u.v./vis. and 1500 and 1250 ± 100 cm^{-1} for fluorescence). The differences in energy between neighbouring peaks in the excited state (measured by u.v./vis. spectroscopy) usually are lower than the energy differences between neighbouring peaks in the ground state (measured by fluorescence spectroscopy). The results here do not necessarily conflict with this generalization, when the limit of accuracy of the peak positions is considered.

Raman spectroscopy

The large amount of fluorescence found in PPV made the measurements difficult so that in the overview Raman spectrum only the peaks at 1172 and 1584 cm^{-1} were easily distinguishable. Therefore, only the spectral ranges from 1100 to 1400 cm^{-1} and from 1500 to 1650 cm^{-1} were studied in detail. The Raman spectra were identical for PPV made from both precursors. Two fairly sharp peaks were observed at 1172 and 1584 cm^{-1} and correspond, respectively, to the centrosymmetric C–H in-plane bend and the double-bond stretch. It may be noted that this mode is similar to the double-bond stretching mode in polydiacetylenes[14–16], except for the replacement of the triple bond with the phenyl ring. Other very weak peaks were found at 1328, 1548 and 1625 cm^{-1} (refs. 15, 16). The peaks at 1172 and 1584 cm^{-1} are in excellent agreement with the differences in energy between the peaks in the u.v./vis. and fluorescence spectra, also providing evidence in favour of the assignment of the peaks in the u.v./vis. and fluorescence spectra to phonon sidebands[14–16]. Because fluorescence and Raman spectroscopy are not very sensitive to the number of uninterrupted arylene vinylene units, the respective spectra for PPV prepared from both the **IIA** and **IIB** precursor polymers were very similar.

Small-angle X-ray scattering (*SAXS*)

The appearance of phonon sidebands in the u.v./vis. spectrum of PPV made from the precursor polymer **IIB** can be explained as resulting from fewer defects in the polymer backbone. As shown in *Figure 4*, the SAXS pattern of PPV made from precursor polymer **IIA**

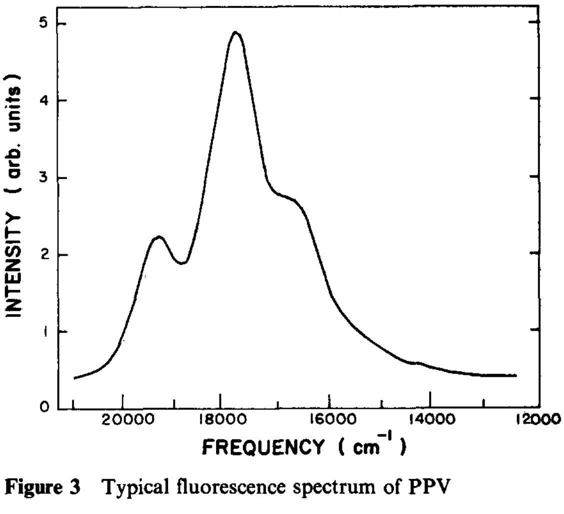

Figure 3 Typical fluorescence spectrum of PPV

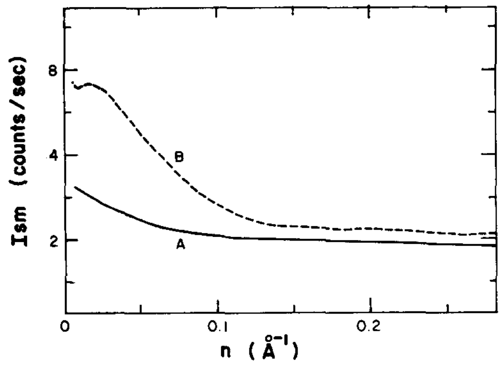

Figure 4 Small-angle X-ray scattering diagrams for PPV, **III**, made from (A) the acyclic sulphonium salt precursor polymer **IIA** and (B) the cyclic sulphonium salt precursor polymer **IIB**

resembles the pattern of an amorphous polymer or, perhaps more precisely, the pattern of an isotropic polycrystalline material[14], but for PPV made from **IIB** the scattering pattern shows a long period spacing of about 400 Å. This relatively higher degree of crystallinity of the latter suggests that there are fewer defects in the PPV when obtained from the cyclic sulphide precursor polymer, **IIB**. It is interesting to note that the relative absorption in the i.r. at 784 cm^{-1} was stronger for PPV films made from the precursor polymer **IIB**. This observation supports the assertion made by Bradley[14] that the i.r. band at 784 cm^{-1} is a crystallinity band.

Cyclic voltammetry

The relative peak positions of cyclovoltammograms of PPV obtained from the acyclic sulphonium salt precursor polymer, **IIA**, taken at various scan speeds for a dichloromethane solution, were in good agreement with the cyclovoltammograms reported by Obzrut and Karasz[7]. At a scan speed of 1 mV s^{-1} an anodic peak was observed at 1.07 V vs. Ag/AgCl (0.97 V vs. SCE), and a cathodic peak was observed at 0.79 V vs Ag/AgCl (0.69 V vs. SCE) ($E_{1/2}=0.80$ V vs. SCE). The absolute values are also in good agreement if the differences in solvent and reference electrode are taken into account.

The cyclovoltammograms of PPV made from the cyclic sulphonium salt precursor polymer, **IIB**, using dichloromethane as the solvent, showed the same results as for PPV made from the acyclic sulphonium salt precursor polymer, **IIA**. At 1 mV s^{-1} an anodic peak was obtained at 1.04 V vs. Ag/AgCl (0.94 V vs. SCE) and a cathodic peak at 0.77 V vs. Ag/AgCl (0.67 V vs. SCE). However, it is important to note that the temperature used for the conversion of **IIB** to **III** was about 100°C lower than that for the conversion of precursor polymer **IIA**. It was possible to obtain a reversible cyclovoltammogram at a sweep speed of 100 mV s^{-1} (see *Figure 5*) with an anodic peak at 1.05 V vs. Ag/AgCl (0.95 V vs. SCE) and a cathodic peak at 0.85 V vs. Ag/AgCl (0.75 V vs. SCE).

The peak positions (vs. SCE) were very similar when the cyclovoltammograms were performed using an acetonitrile solution. For PPV made from both precursors, an irreversible peak at about 1.6 V was observed. This peak is consistent with that reported by Obzrut and Karasz[7]. According to Hörhold and coworkers[17], the second peak results from the formation of a dication (bipolaron). The value for the oxidation potential is also in good agreement with the theoretically predicted value of 0.7 V vs. SCE, and the value of 0.76 V vs. Ag/AgCl reported by Hörhold and coworkers[8].

The reduction potentials for PPV made from both precursors were also very similar. As shown in *Figure 6*, the reduction potential of PPV was found to be −1.80 V vs. Ag/AgCl (−1.85 V vs. SCE) with peaks at −1.78 V vs. Ag/AgCl and −1.81 V vs. Ag/AgCl (−1.83 and −1.86 V vs. SCE, respectively). The value of −1.85 V vs. SCE for the reduction potential is also in good agreement with the theoretical value of −1.8 V vs. SCE calculated by Bredas[4], and the value of −1.76 V vs. Ag/AgCl reported by Hörhold and coworkers[8].

Oxidation potential of I^- and I_3^-

The oxidation potentials of I^- and I_3^- were measured under the same conditions described in the 'Experimental' section by dissolving about 20 mg of tetrabutylammonium iodide in the cell solution and then adding increasing amounts of iodine, to convert all the iodide to triiodide before each measurement. The following peaks with their

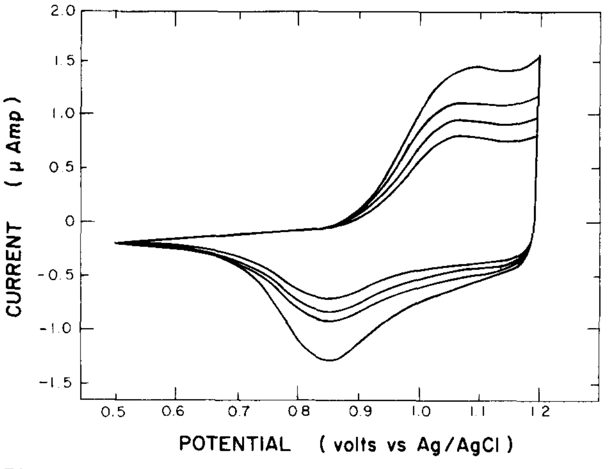

Figure 5 Sequential cyclovoltammograms of a thin film of PPV, **III**, made from the cyclic sulphonium salt precursor polymer **IIB** at a sweep speed of 100 mV s^{-1}

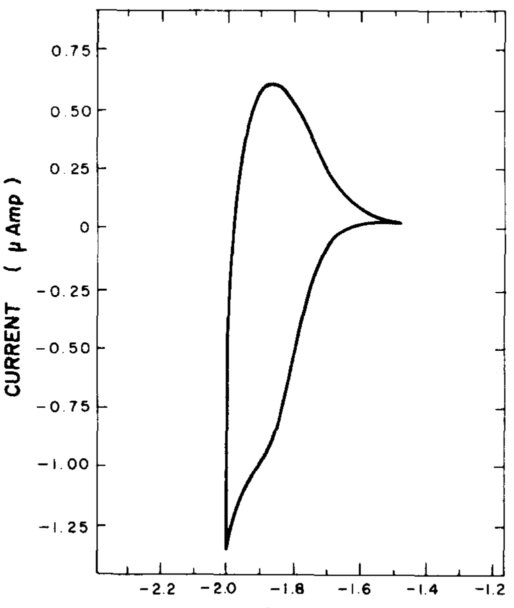

Figure 6 Reduction potential of PPV, **III**, made from the cyclic sulphonium precursor polymer **IIB** at a sweep speed of 1 mV s^{-1}

respective oxidation reactions were observed when no iodine was added to the solution under study:

$$6I^- \rightarrow 2I_3^- + 4e^- \qquad E_{1/2} = 0.35 \text{ V vs. SCE}$$

$$2I_3^- \rightleftharpoons 3I_2 + 2e^- \qquad E_{1/2} = 0.50 \text{ V vs. SCE}$$

The irreversible peak at 0.35 V vs. SCE completely disappeared when about a 3 M excess of iodine was added to the solution, and the $E_{1/2}$ at 0.50 V shifted slightly to 0.52 V and remained there even after large amounts (10 M excess) of iodine were added, which is consistent with previous results[18].

Oxidation equilibrium constant

Because the oxidation potentials for I_3^- and PPV are known, it is now possible to estimate the equilibrium constant for the oxidation of PPV with iodine. The following equation:

$$2\text{PPV} + 3I_2 \rightleftharpoons 2\text{PPV}^{\cdot +} + 2I_3^- \qquad (1)$$

can be written as the difference of the following half-cell reduction potentials[19]:

$$3I_2 + 2e^- \rightleftharpoons 2I_3^- \qquad E_{1/2} = 0.52 \text{ V vs. SCE} \qquad (2)$$

$$\text{PPV}^{\cdot +} + e^- \rightleftharpoons \text{PPV} \qquad E_{1/2} = 0.80 \text{ V vs. SCE} \qquad (3)$$

By multiplying equation (3) by a factor of 2 (that is, $n=2$, the number of electrons), and by subtracting equation (3) from equation (2), the following estimates are obtained for the Gibbs free energy of reaction and the equilibrium constant, K:

$$\Delta G = -nFE = -2 \times 96.485 \times (-0.28)$$

$$= +55 \text{ kJ mol}^{-1} \qquad (4)$$

from which:

$$\ln K = nFE/RT = -55/RT = -22 \qquad (5)$$

and:

$$K = 2.3 \times 10^{-10} \qquad (6)$$

where F = Faraday's constant = 96.485 kC mol^{-1}, R = gas constant = 0.008 314 kJ mol^{-1} K^{-1} and T = 300 K.

The extremely low value of the equilibrium constant, indicative of a high positive Gibb's free energy of reaction, rules out the possibility of PPV being oxidized with iodine to any extent even when the energy gained from the formation of I_3^- in the solid state is considered. If a reasonable value of 10^{-3} V °C^{-1} is taken for the temperature dependence of the overall cell voltage $\langle (dE/dT)_P \rangle$[19], the equilibrium constant K will reach a value of 1 at approximatly 300°C (600 K), and this fact could explain some observed phenomena[5].

The cyclovoltammograms of the acyclic sulphonium salt precursor polymer **IIA**, which had been heated to 80 and 150°C for 24 h *in vacuo*, showed no oxidation behaviour, so it is essentially impossible to form a significant number of charge-transfer complexes within the films treated under these conditions with iodine. There is some evidence[5], according to i.r. results, of a charge-transfer reaction characteristic of oxidation between partially converted precursor **IIA** polymer films. Further study is required to resolve this discrepancy. However iodine could have reacted with either the halide counterion, the sulphonium group, or the benzylalkyl sulphide, or the iodine could be 'soluble' in the precursor films. PPV made from the cyclic sulphonium salt precursor polymer **IIB** showed no appreciable conductivity increase (at least much less than 10^{-6} S cm^{-1}) when treated with iodine.

SUMMARY AND CONCLUSIONS

The visible part of the u.v./vis. spectrum of PPV, **III**, made via the cyclic sulphonium salt precursor polymer **IIB**, showed phonon sidebands at room temperature because of the absence of harmful side-reactions in the conversion of the precursor polymer to PPV; that is, side-reactions that would disrupt polymer crystallite formation. The phonon sidebands become even more sharply defined at liquid-nitrogen temperatures. The u.v./vis. spectrum of PPV obtained from the cyclic sulphonium salt precursor polymer **IIB** is the most structured u.v./vis. spectrum ever reported for PPV. The value for the band-gap energy is in excellent agreement with the value calculated by theory.

The values of the oxidation and reduction potentials for PPV obtained from both precursors are in good agreement with the value estimated by theory and previous literature reports. The instability of the oxidized polymer and the poor conductivities obtained when PPV is treated with iodine result from the high oxidation potential of PPV.

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